

III.A.9 Novel Sulfur-Tolerant Anodes for Solid Oxide Fuel Cells

Objectives

- Characterize the effect of sulfur poisoning on solid oxide fuel cell (SOFC) performance and its recovery process under various operating conditions.
- Investigate the detailed mechanisms for sulfur poisoning of nickel-based anodes in SOFCs.
- Establish scientific principles for rational design of sulfur tolerant anodes.
- Explore new sulfur tolerant anode materials to meet SECA program objectives.

Accomplishments

- Revealed the effects of cell operating conditions [including temperature, hydrogen sulfide (H_2S) concentration, cell voltage/current density, etc.] on sulfur poisoning and recovery of nickel-based anode in SOFCs.
- Demonstrated experimentally that sulfur poisoning of nickel-yttria stabilized zirconia (Ni-YSZ) anodes is not due to formation of conventional nickel sulfides.
- Characterized in real time the nickel sulfide formation process on the surface of a Ni-YSZ electrode and the corresponding morphology change as the sample was cooled in H_2S -containing fuel.
- Predicted sulfur tolerance and catalytic activity towards hydrogen oxidation for various transition metals/alloys.
- Fabricated new anode materials that exhibit excellent tolerance to H_2S and promising cell performance.

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Introduction

One of the unique advantages of SOFCs over other types of fuel cells is the possibility of direct internal reforming of commercial hydrocarbon fuels, thereby eliminating the need for a separate fuel processing subsystem. However, all fossil fuels contain some sulfur compounds, which are converted to gaseous H_2S in the reforming process. Current SOFC anodes have very limited tolerance to H_2S . As a result, the H_2S concentration in the feed fuel must be reduced to less than 1 ppm (by volume) for optimum performance, which increases the complexity of the system and the cost of operation. Although considerable efforts have been devoted to the development of sulfur-tolerant anode materials, a detailed understanding of the sulfur poisoning process and its mechanism is still lacking, and there is no anode material that is both sulfur-tolerant and compatible with current cell materials/fabrication techniques. The design of new materials largely proceeds via trial-and-error, without much theoretical guidance.

In view of these deficiencies, this project focuses on (i) investigating the poisoning process of Ni-based anodes by H_2S in SOFCs and understanding the poisoning mechanism, (ii) developing new anode materials that have better sulfur tolerance and comparable performance with current Ni-based anodes, and (iii) establishing scientific principles that may guide the selection of candidate sulfur resistant anode materials for SOFCs.

Approach

The cell current at a constant voltage was monitored continuously when H_2S gas (at the ppm level) was introduced and removed from the fuel flow under different conditions (temperature, H_2S concentration and cell current density/voltage, etc.). The impedance responses of the cell under open-circuit conditions were also measured in fuels with and without H_2S to determine the contributions from the electrolyte and different interfaces. The sulfur-anode interaction was investigated by characterizing the chemical and structural changes on the surface of dense Ni-YSZ composites. This includes *in situ* Raman spectroscopy, in which the Raman signal and structure at elevated temperatures were obtained on a real-time basis when H_2S was introduced and removed from the Raman cell. The results from *in situ* Raman spectroscopy were

also correlated with other ex-situ techniques such as scanning electron microscopy (SEM), energy dispersive x-ray (EDX), and x-ray diffraction (XRD), etc. to study the sulfur-anode interaction.

Meanwhile, quantum-chemical calculations were used to predict the adsorption energy and bond length for sulfur and hydrogen atoms on various metal surfaces. The results were used to predict sulfur tolerance and anode activity toward electrochemical oxidation of H_2 fuel for those different materials. An impregnation method was used to introduce the precursors for sulfur-resistant anodes into a porous YSZ layer bonded onto a dense YSZ electrolyte. The anode was reduced in-situ and tested in fuels with H_2S under various conditions.

Results

Sulfur poisoning of the Ni-YSZ cermet anode for SOFCs consists of two stages. The first is a rapid degradation within a few minutes that causes the majority of the decrease in performance, followed by a gradual degradation that occurs over several hours or even days. The extent of degradation is influenced by cell voltage (or, alternatively, the cell current density). The higher the cell current density (or the lower the cell operating voltage), the lower the extent of sulfur poisoning. The recovery of the poisoned anode can be realized by continuous flowing of sulfur-free fuel, and the recovery is faster when the cell current density is higher [Figure 1(a)]. Impedance studies show that the degradation in cell performance was caused by a large increase in anode interfacial resistance while there is no significant change in bulk resistance [Figure 1(b)]. The anode interfacial resistance increases as H_2S concentration increases [Figure 1(c)]. Correspondingly, at certain temperature and cell voltage, the extent of sulfur poisoning increases with increasing H_2S concentration until saturation is reached. With the same concentration of H_2S , the extent of sulfur poisoning increases dramatically with decreasing temperature. The lowest tolerable H_2S level also decreases dramatically with decreasing temperature [Figure 1(d)].

In situ Raman spectroscopy experiments show no sign of conventional nickel sulfide formation on the surface of the Ni-YSZ composite and there is also no significant change in surface morphology when the sample is exposed to fuels containing 50 ppm H_2S at high temperatures ($>500^\circ C$). However, when the Ni-YSZ composite sample was cooled down in H_2S -containing fuels, conventional nickel sulfide (e.g., Ni_3S_2) gradually forms on the Ni surface, accompanied by dramatic change in surface morphology [Figures 2(a) and 2(b)]. When the sample is cooled down completely, the surface of Ni particles is full of ball-

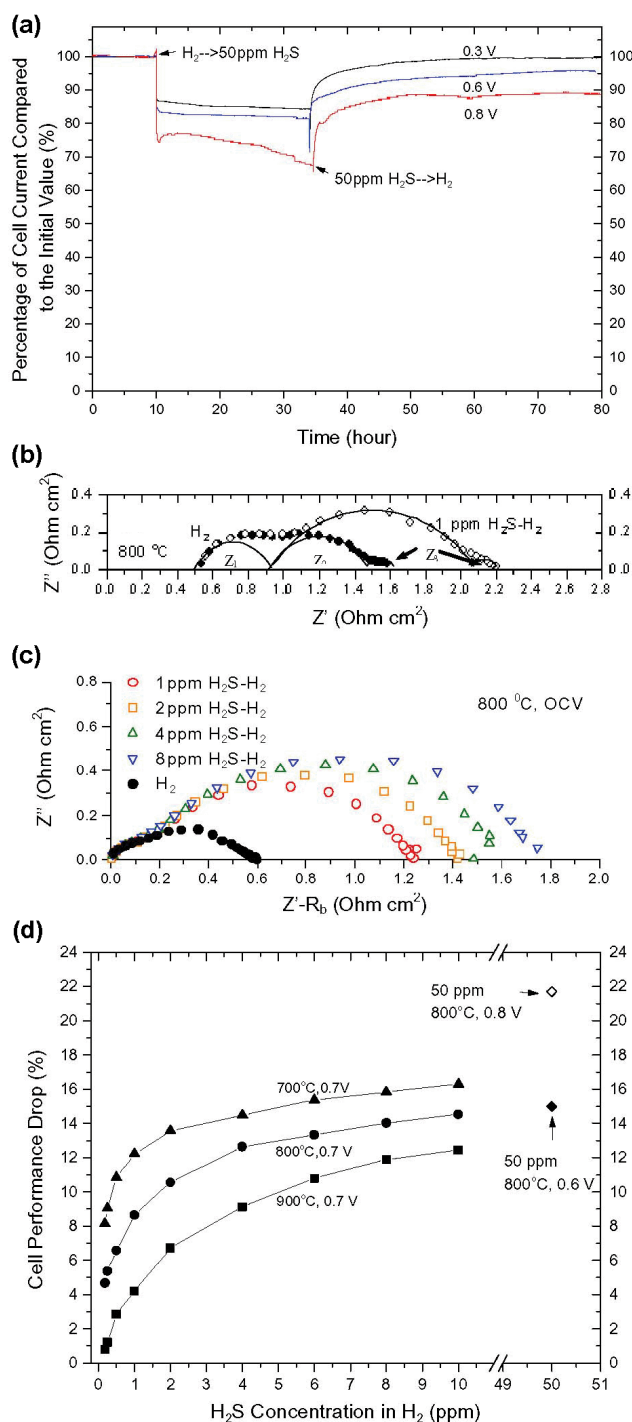


FIGURE 1. (a) Influence of cell voltage on sulfur poisoning and regeneration for Ni-YSZ cermet anode at 800°C; (b) change in impedance spectrum for a cell measured at OCVs using 2-electrode configuration in fuels with and without 1 ppm H_2S ; (c) change in impedance spectrum for the anode/electrolyte interface measured at OCV using 3-electrode configuration in fuels with different concentration of H_2S ; (d) influence of H_2S concentration on the extent of sulfur poisoning for Ni-YSZ anode at different temperatures. R_b represents the ohmic resistance of the cell and $Z' - R_b$ the anode polarization resistance of the cell.

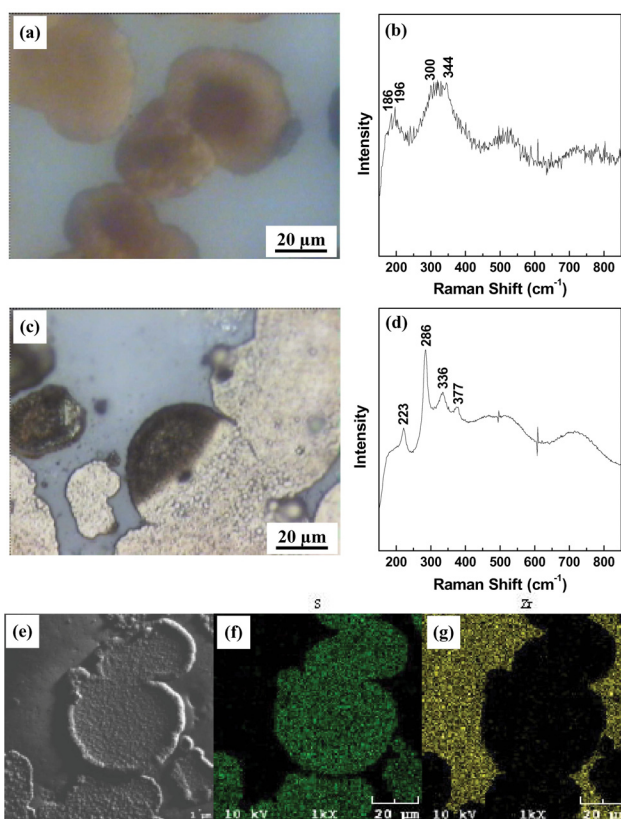


FIGURE 2. Optical microscopy image (a) and corresponding Raman spectrum from the Ni region (b) for the Ni-YSZ composite in *in situ* Raman experiment at 216°C in a fuel with 50 ppm H₂S; optical microscopy image (c), corresponding Raman spectrum taken from the Ni region (d), SEM image (e), S elemental map (f) and Zr element map (g) for the Ni-YSZ composite heated treated at 600°C in 50 ppm H₂S/50% H₂/1.5% H₂O/48.5% N₂ for 20 h.

like and/or edge-like structures as shown in Figures 2(c) and 2(e). The Raman spectra give sharp peaks corresponding to Ni_xS_y. The distribution of sulfur on the Ni-YSZ composite is confined to the Ni region [Figures 2(e) – 2(f)]. This preliminary study indicates that the fundamental reasoning for sulfur poisoning is most likely sulfur adsorption on the anode. Cooling of the anode in H₂S-containing fuel (even in the ppm range) should be avoided since it causes formation of bulk nickel sulfides and irreversible morphology changes.

Quantum-chemical calculations have been used to estimate the adsorption energy of sulfur species and hydrogen on different transition metal surfaces. Figure 3 shows the normalized adsorption energy for H₂S and H₂ on various transition metals surfaces obtained from quantum-chemical calculations. According to the study, the adsorption of sulfur on metals such as Ag, Cu, V, Cr and Mo is significantly weaker compared with Ni, suggesting possible sulfur tolerance for these materials. New sulfur-resistant anodes have been prepared using impregnation methods. They demonstrate acceptable

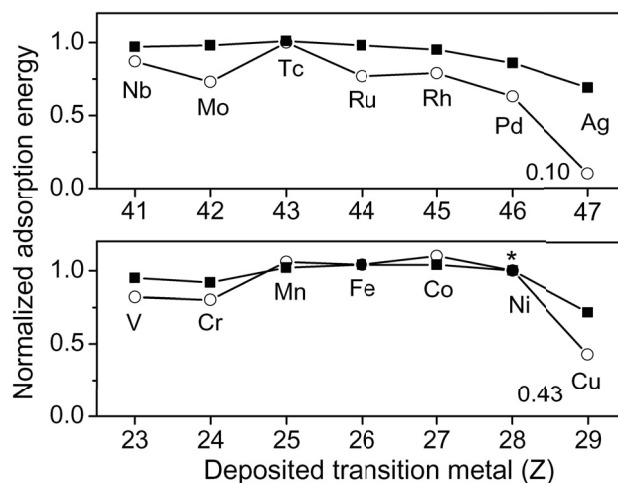


FIGURE 3. Comparison of Predicted Molecular Adsorption Energies for H₂S (open circle) and Dissociative Adsorption Energies for H₂ (closed square) on Modified Ni Surfaces

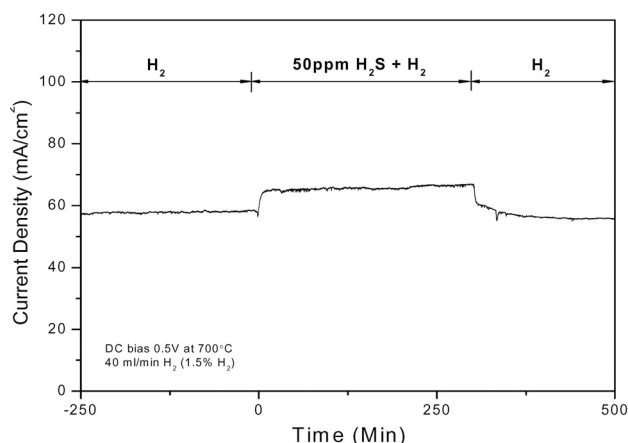


FIGURE 4. Change of Current Density versus Time for Cells with New Anode When 50 ppm H₂S Was Introduced into and Removed from the Fuel

cell performance and excellent sulfur tolerance or even sulfur enhancement behavior in fuels with H₂S concentration up to 50 ppm, as shown in Figure 4.

Conclusions and Future Directions

The sulfur poisoning and recovery for SOFC Ni-YSZ anodes is strongly influenced by operating parameters such as temperature, H₂S concentration, and cell current density/voltage. Generally, sulfur poisoning is more severe at lower temperature, higher H₂S concentration or lower cell current density (higher cell voltage). The *in situ* Raman spectroscopy experiment suggests that sulfur poisoning is not likely to be caused by formation of conventional sulfide. However, bulk sulfides do form at lower temperature (<400°C) in fuels with H₂S in the

ppm range, also causing dramatic morphology changes at the Ni surface. Quantum-chemical calculations suggest that some metals such as Ag, Cu and Mo have lower sulfur adsorption energy and are potential candidate materials for sulfur resistant anodes for SOFCs. Based on the theoretical calculations, new anodes have been prepared using impregnation methods. Initial testing indicates that the new anode materials display reasonable activity and excellent sulfur tolerance (or even sulfur enhancement) in fuels containing up to 50 ppm of H₂S.

Future work is briefly outlined as follows:

- Improve the sensitivity of detecting specific adsorbed sulfur species on Ni anodes using *in situ* Raman spectroscopy. Characterize the depth profile of sulfur in the anode surface layer after exposure to H₂S for different periods of time.
- Determine the time evolution of surface reactive sites, surface species, and anode microstructure during long-term (>10³ hours) exposure to H₂S contaminated fuel.
- Use the experimentally observed correlations and deduced mechanisms of sulfur-anode interactions to predict the long term stability of Ni/YSZ anodes when exposed to low level H₂S contamination (<10 ppm).
- Establish an effective operational window (in terms of temperature, H₂S concentration, cell voltage, etc.) for SOFCs fed with sulfur-containing fuels.
- Suggest possible modifications to the baseline Ni-YSZ anode materials set that might increase the performance stability and lifetime tolerance to sulfur contaminated fuels.
- Develop new sulfur-resistant anode materials with better sulfur tolerance and long-term stability.

FY2006 Publications/Presentations

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2. Z. Cheng, S. Zha, L. Aguilar, D. Wang, J. Winnick, and M. Liu, "A Solid Oxide Fuel Cell Running on H₂S/CH₄ Fuel Mixtures," *Electrochemical and Solid State Letters*, **9**, A31-A33 (2006).
3. Z. Cheng, S. Zha, and M. Liu, "Stability of Materials as Candidates for Sulfur-Resistant Anodes of Solid Oxide Fuel Cells," *Journal of The Electrochemical Society*, **153**, A1302-A1309 (2006).
4. Y. M. Choi, C. Compson, Charles, M. C. Lin, M. Liu, "A mechanistic study of H₂S decomposition on Ni- and Cu-based anode surfaces in a solid oxide fuel cell," *Chemical Physics Letters*, **421**, 179-183 (2006).
5. Y. M. Choi, C. Compson, M.C. Lin, and M. Liu, "Ab initio analysis of sulfur tolerance of Ni, Cu, and Ni-Cu alloys for solid oxide fuel cells," *Journal of Alloys and Compounds*, in press.
6. J. Dong, Z. Cheng, S. Zha, and M. Liu, "Identification of Nickel Sulfides on Ni-YSZ Cermet Exposed to H₂ Fuel Containing H₂S Using Raman Spectroscopy," *Journal of Power Sources*, **156**, 461-465 (2006).
7. J. Dong, S. Zha, and M. Liu, "Study of Sulfur-Ni Interactions using Raman Spectroscopy", in: *Proceedings of 207th ECS Meeting*, 2005.
8. S. Zha, P. Tsang, Z. Cheng, and M. Liu, "Electrical properties and sulfur tolerance of La_{0.75}Sr_{0.25}Cr_{1-x}Mn_xO₃ under anodic conditions," *Journal of Solid State Chemistry*, **178**, 1844-1850 (2005).
9. S. Zha, Z. Cheng, and M. Liu, "A Sulfur-Tolerant Anode for SOFCs Gd₂Ti_{1.4}Mo_{0.6}O₇," *Electrochemical and Solid State Letters*, **8**, A406-A408 (2005).
10. S. Zha, Z. Cheng, and M. Liu, "Sulfur Poisoning and Regeneration of Ni-based Anodes in Solid Oxide Fuel Cells", *Journal of The Electrochemical Society*, submitted.